

ADA013446

FA-TA-75048

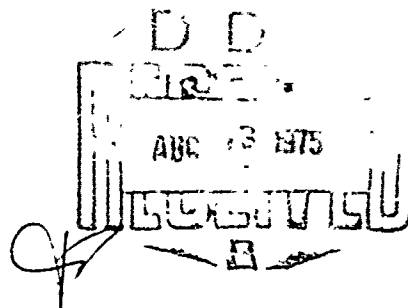
AD

AUTORADIOGRAPHIC DETERMINATION OF THE Di-n-butyl  
PHTHALATE CONCENTRATION PROFILE IN A  
NITROCELLULOSE MATRIX

July 1975

12

Approved for public release; distribution unlimited.



Munitions Development & Engineering Directorate

U.S. ARMY ARMAMENT COMMAND  
FRANKFORD ARSENAL  
PHILADELPHIA, PENNSYLVANIA 19137

## DISPOSITION INSTRUCTIONS

Destroy this report when it is no longer needed. Do not return it to the originator.

DISPOSITION FOR	
RTIS	White Section <input checked="" type="checkbox"/>
D C	Red Section <input type="checkbox"/>
UNP. COPIES	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	ACAIL. AND/OR SPECIAL
Aro	

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 14 FA-TA-75048	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) AUTORADIOGRAPHIC DETERMINATION OF THE 'Di-n-butyl' PHTHALATE CONCENTRATION PROFILE IN A NITROCELLULOSE MATRIX,	5. TYPE OF REPORT & PERIOD COVERED Technical Engineering rept. Abstract	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) B.W. Brodman M.P. Devine R.W. Finch M.S. MacClaren Olin Corporation, Chemicals Group, New Haven, CT 06504	8. CONTRACT OR GRANT NUMBER(s) DL 81	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS AMCMS: 611102.11.857 DA: 1T161102A32C03
9. PERFORMING ORGANIZATION NAME AND ADDRESS FRANKFORD ARSENAL Attn: SARFA-MDP-R Philadelphia, PA 19137	11. CONTROLLING OFFICE NAME AND ADDRESS Picatinny Arsenal 11 14 May 74	12. REPORT DATE July 1975 13. NUMBER OF PAGES 10
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) DA-I-T-161102-A-32--	15. SECURITY CLASS. (of this report) UNCLASSIFIED	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. 17 1-T-161102-A-32-C-031		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Propellant Manufacture      Small Arms Deterrents Small Arms Propellant      Hydrogen Bonding Propellant Combustion		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The concentration profile of a deterrent (di-n-butyl phthalate) which had been diffused into a nitrocellulose sphere (ball propellant) containing nitroglycerin was studied by means of autoradiography. Results indicate a level concentration part way into the sphere with an abrupt dropoff in concentration. An explanation for this type of concentration profile is offered based on hydrogen bonding of the deterrent carbonyl group with un-esterified hydroxyl groups in nitrocellulose.		

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

## Autoradiographic Determination of the Di-*n*-butyl Phthalate Concentration Profile in a Nitrocellulose Matrix

B. W. BRODMAN and M. P. DEVINE, *Munitions Development and Engineering Directorate, Frankford Arsenal, Philadelphia, Pennsylvania 19137*, and R. W. FINCH and M. S. MACCLAREN, *Olin Corporation, Chemicals Group, New Haven, Connecticut 06504*

### Synopsis

The concentration profile of a deterrent (di-*n*-butyl phthalate) which had been diffused into a nitrocellulose sphere (ball propellant) containing nitroglycerin was studied by means of autoradiography. Results indicate a level concentration part way into the sphere with an abrupt dropoff in concentration. An explanation for this type of concentration profile is offered based on hydrogen bonding of the deterrent carbonyl group with unesterified hydroxyl groups in nitrocellulose.

### INTRODUCTION

Deterrents are compounds which are diffused some distance into small-arms propellant grains to reduce their initial burning rate (when the propellant bed surface area is large). This reduction is accomplished by the endothermic decomposition of the deterrent. A knowledge of the concentration profile of deterrent in the propellant grain is important for manufacturing purposes as well as for prediction of ballistic performance. Several studies<sup>1,2,3</sup> have described methods for determining depth of deterrent penetration into small-arms propellant grains. However, these methods were not directly capable of measuring the concentration profile of deterrent in the grain. The first study<sup>1</sup> described a technique wherein a crystal violet dye is used to stain sectioned extruded propellant grains giving a purple color to the deterrent, permitting depth measurement.

A similar study<sup>2</sup> was made of nitroglycerin and dibutyl phthalate (DBP, a deterrent) penetration in ball propellant by using a visual boundary microscopically observed in sectioned ball propellant grains. By comparison with other studies dealing with diffusion of plasticizers into polymers, it was assumed that this observed optical boundary corresponded to a sharp concentration gradient associated with the DBP diffusion front. Also, it was inferred that a shallow plasticizer concentration gradient existed from the grain surface to the diffusion front.

A third study<sup>3</sup> in this area was concerned with correlation of DBP penetration depth with propellant burning rate. The penetration depth was

determined by using a crystal violet stain on grain segments, similar to the procedure described in reference 1. In the past, no direct measuring technique has been used to establish the concentration of DBP in the deterred region of the propellant grain. For this reason, a scaled-down production procedure was used to deter spherical nitrocellulose propellant grains (containing nitroglycerin) with  $^{14}\text{C}$ -labeled DBP. Autoradiographs were then taken of the center section of these grains. The concentration profile of DBP in these spherical nitrocellulose grains was then determined from the autoradiographic data.

### EXPERIMENTAL

**Propellant.** The ball propellant used for this study was WC 870, which was manufactured by Olin Corporation. It contained 10% impregnated nitroglycerin, and the size of the balls ranged from 0.0342 to 0.0257 in.

**Detering Process.** Ball powder, 1.2 g, and 3.6 ml water were slurried in a test tube. The slurry was brought to 76°C in a constant-temperature bath and at the minimum stirring rate necessary to keep the ball powder suspended. Separately, an emulsion of DBP, Swift Colloid #1 (Swift & Co.), and water was prepared as follows: 0.1 g Swift Colloid #1 is added to 50 ml water and mixed until homogeneous; 1.00 ml was then mixed with 0.58 ml "cold" DBP and 0.020 ml tagged DBP (carboxyl 7-C-14, New England Nuclear, 1.00 millicurie). This mixture was brought to 76°C in the constant-temperature bath alongside the ball powder slurry. After vigorous agitation to uniformly distribute the DBP throughout the emulsion, an appropriate amount of emulsion was introduced into the ball powder slurry. The resulting mixture was then stirred at constant temperature. After 6 hr, the slurry was removed from the bath, the emulsion poured off, and the powder rinsed several times with a total of 40 ml water. The resulting deterred propellant was then air dried for a minimum of 72 hr at ambient temperature in a covered petri dish.

**Microtoming.** In preparation for microtoming the ball propellant, grains were mounted on a  $1/8$ -in.-diameter ceramic rod with a drop of Titebond glue manufactured by the Franklin Glue Co. (It had been determined that the glue contained no solvents which could alter the deterrent penetration characteristics.) The glue was allowed to set for 24 hr before sectioning.

A section thickness of 30  $\mu$  was found to be most suitable for the autoradiography. In order to obtain a section from near or at the center of the grain, the ball was microtomed until less than half remained, and the largest diameter section was taken to be the center section. To avoid contamination of the sample by the microtome blade, it was washed with  $\text{CHCl}_3$  after using and stored to a new position.

**Autoradiography.** The center segment of the deterred propellant grains was mounted on a microscope slide with a drop of Titebond glue. A transfer solution for the AR-10 (Kodak Ltd., London) film was prepared as

recommended by Kodak. Sucrose, 20 g, and 0.01 g potassium bromide were dissolved in 1 liter water. (This solution should be used immediately and prepared fresh on a daily basis.)

The slide with the mounted ball propellant segment was then covered with AR-10 film. A section of the film large enough to cover the specimen and overlap the edge of the slide was cut from the film plate. This film was then floated emulsion side down on the transfer solution such that the specimen was in contact with the photographic emulsion. The slide was then air dried at ambient temperature and stored during the exposure period (144 hr) in a light-tight box at 4°C.

After exposure, the AR-10 film was developed with gentle agitation for 5 min in D-19 developer (Kodak), washed in water for 1 min, and fixed in Acid Fixer (Kodak) for 6 min. After washing in water for 20 min, the film was transferred to a clean slide.

**Photomicrography.** Ball propellant segments were photographed utilizing bright field conditions through a Leitz Wetzlar Ortholux microscope equipped with a 5× eyepiece and 4× objectives lens. The camera used was a Nikon F2 with adapter and was loaded with Plus X-Pan film (Kodak-ASA 125). Exposures of  $\frac{1}{4}$  sec were used.

Autoradiographs were photomicrographed using dark-field conditions with a 10× objective and a 5× eyepiece utilizing the previously described Nikon system. Exposures of 10 sec were used. The effective magnification obtained from the 10× objective was 32×.

In all cases, the Plus X-Pan film was developed for 8 min in a 1:1 water dilution of DK-50 developer (Kodak). Films were washed in water for 1 min, fixed for 6 min in Acid Fixer, and washed in running water for 20 min. The resulting negatives were air dried overnight.

**Densitometry.** The photomicrographs of the autoradiographs taken with the 10× objective were found to give images suitable for scanning on the Applied Research Laboratories Recording Densitometer. The densitometer output is a strip chart giving relative optical density. Each "densitometer unit" from the strip chart recording represents 4.34  $\mu$  on the autoradiographs taken with the 10× objective. The optical density measurements obtained from the densitometer scans were then converted to absorbance by running a series of standard filters on the densitometer and calibrated Perkin-Elmer Model 323 UV-VIS spectrophotometer. Relative transmittance was thus converted to absolute transmittance and then to absorbance using

$$\text{Absorbance} = -\log (\text{transmittance}).$$

The absorbance was then plotted versus "densitometer units" to illustrate the concentration gradient of DBP along a radius of the propellant grain.

### ERROR DISCUSSION

There were several potential error sources which include  $\beta$ -scattering and self-absorption. These will be discussed individually.

**$\beta$ -Scattering.** With the AR-10 emulsion (used in this study), more than 96% of the exposed silver grains will be contained within  $5\ \mu$  of the source. This gives a resolution of about  $10\ \mu$  on the autoradiograph and is the largest source of error involved in this investigation.

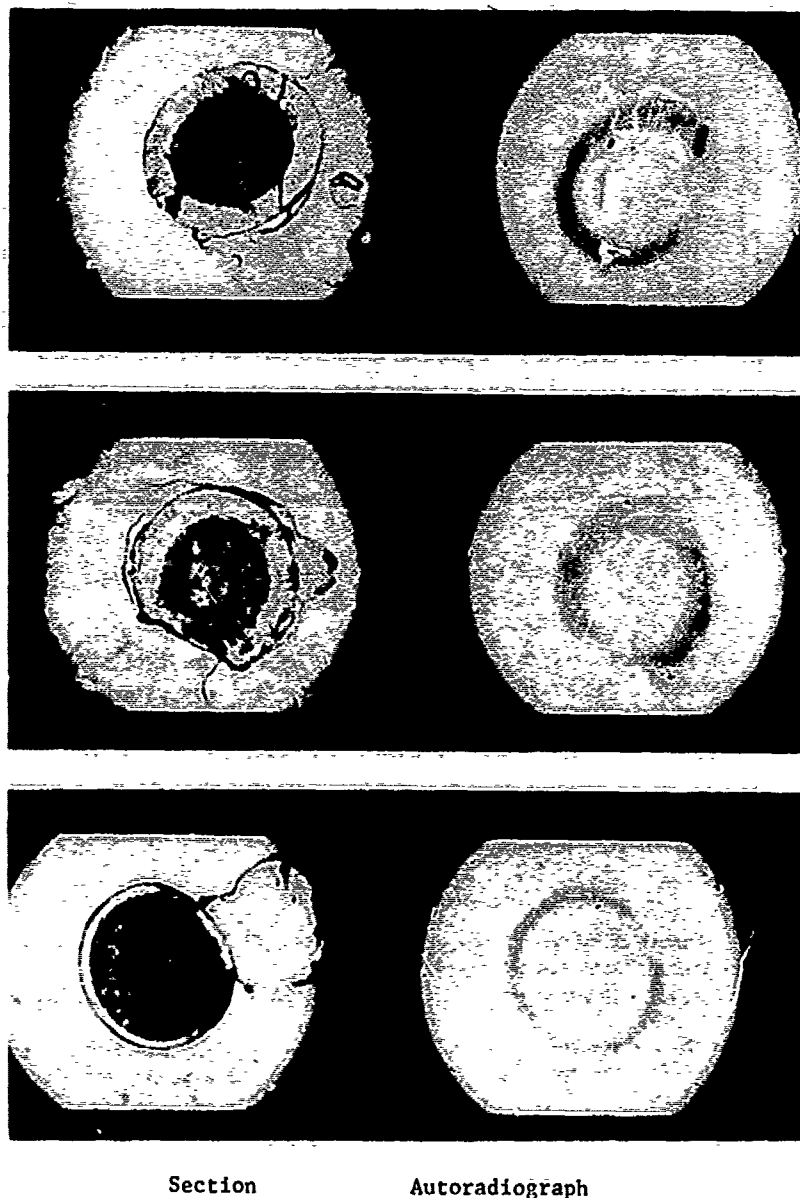
**Self-Absorption.** It has been found that some  $\beta$ -particles will penetrate up to  $30\ \mu$  of nitrocellulose and still be capable of exposing the photographic emulsion. This indicates that  $\beta$ -particles will not be completely absorbed by the surrounding nitrocellulose and will lead to exposure of the film outside the area actually containing DBP. This condition leads to difficulty in defining the inner boundary of DBP penetration.

**Film Configuration.** The AR-10 film may drape itself over the samples in several ways. One of those configurations creates a boundary line in the developed autoradiograph at the segment's outer edge. Other configurations did not allow such exact determination of the outer edge of the segment. Fortunately, the most predominant configuration encountered is the former which allowed relatively clear definition of the outer segment edge on the autoradiographs.

**Film Shrinkage.** AR-10 film was found to shrink about 10% generally and occasionally as much as 15%, though this much shrinkage was rare. It was found that the film shrinkage did not affect the results of this study.

## RESULTS AND DISCUSSION

$^{14}\text{C}$ -labeled DBP was diffused into nitrocellulose spheres utilizing a scaled-down production technique. The resulting deterred propellant grains were microtomed, and the center sections were placed in contact with a photographic emulsion. Resulting autoradiographs were photographed through a microscope, and DBP concentration profile data was obtained by scanning the autoradiographs with a densitometer. Figure 1 shows typical autoradiographs of a deterred nitrocellulose grain along with their optical images. Figure 2 shows a composite representation of data obtained for 80 grains after 144 hr of exposing the grains to the photographic emulsion. It appears that there is a level concentration of deterrent through a region of the propellant grain with an abrupt drop in concentration. Further, it can be seen that the depth of deterrent penetration observed visually directly corresponds to that observed on the autoradiograph. It is interesting that the observed concentration profile does not correspond to a classical diffusion case which would initially predict an exponential concentration decrease from the surface inward that would, with time, tend to become level and penetrate through the entire grain. Several recent studies<sup>4,5</sup> have dealt with the hydrogen bonding of deterrents to unesterified hydroxyl groups in nitrocellulose and hydrogen bonding between OH groups in nitrocellulose. It has been shown that DBP does hydrogen bond to unesterified hydroxyl groups in nitrocellulose and that this interaction is stronger than the hydroxyl nitrocellulose interaction. Based on the results obtained in this study, coupled with the hydrogen



Section

Autoradiograph

Fig. 1. Photomicrographs of ball propellant segments containing labeled di-*n*-butyl phthalate and corresponding autoradiographs.

bonding information, it appears that detergent penetration into a propellant matrix is best described by a diffusion with interaction mechanism. In such a mechanism, DBP moves into the propellant grain by diffusion, and molecules are removed from the diffusion stream by hydrogen bonding between the carbonyl group of the detergent and unesterified hydroxyl groups

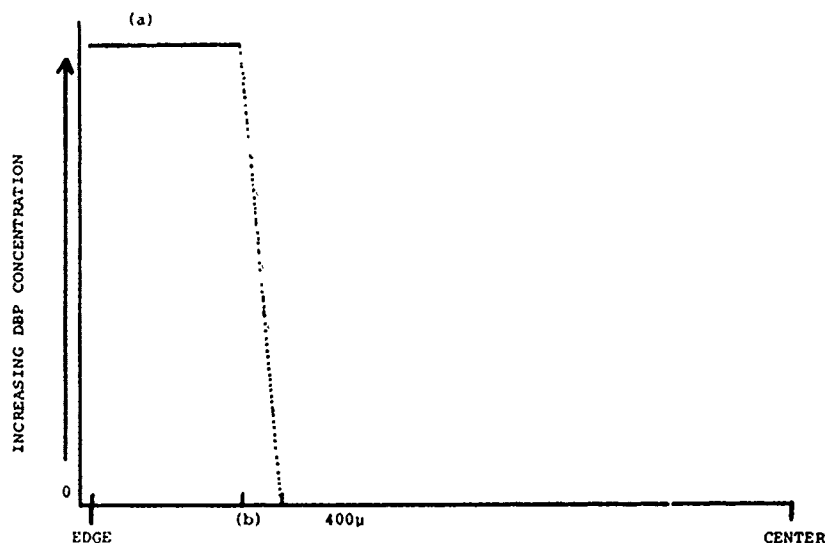


Fig. 2. Concentration of di-*n*-butyl phthalate as a function of distance into a nitrocellulose sphere.

in the nitrocellulose. This mechanism would lead to the level concentration and abrupt drop in concentration observed in the present study.

Further, it appears that the deterrent carbonyl-nitrocellulose hydroxyl interaction is sufficiently strong to prevent leveling of the concentration throughout the grain at ambient or slightly higher temperatures. However, DBP migration has been noted in nitrocellulose-nitroglycerin systems exposed to extreme storage temperatures.

### References

1. J. B. Quinlan, A Microscopic Examination of Extruded Double Base Propellant, Frankford Arsenal Report R-1302, Dec. 1955.
2. M. E. Levy, Microscopic Studies of Ball Propellant, Frankford Arsenal Report R-1286, Sept. 1955.
3. A. H. Milford, Further Studies on the Diffusion of Nitroglycerine and Dibutyl Phthalate Into Ball Powder, Winchester-Western Div. Technical Report No. WWR-68-2, Jan.-Dec. 1967.
4. B. W. Brodman, M. P. Devine, and M. T. Gurbarg, *J. Appl. Polym. Sci.*, **18**, 943 (1974).
5. B. W. Brodman, M. P. Devine, and M. T. Gurbarg, *J. Macromol. Sci.-Chem.*, in press.

Received May 14, 1974

Revised June 10, 1974

# DISTRIBUTION

Commander  
U.S. Army Materiel Command  
5001 Eisenhower Avenue  
Alexandria, VA 22333

1 Attn: AMCDL,  
Dr. Dillaway

1 Attn: AMCDL,  
Dr. Crenshaw

1 Attn: AMCRD,  
Dr. Kaufman

1 Attn: AMCRD-W,  
Weapons Division

1 Attn: AMCRD-T,  
Dr. El Bisi

1 Attn: AMCRP-D,  
Dr. Dellastatious

1 Attn: AMCPM,  
Project Manager

1 Attn: AMCRD-MT

1 Attn: AMCRD-TC

1 Attn: AMCRD-TE

1 Attn: AMCRD-TP

1 Attn: AMCDL

Commander  
U.S. Army Test & Evaluation Command  
Aberdeen Proving Ground, MD 21005

1 Attn: AMSTE-BC

1 Attn: AMSTE-BG

1 Attn: Technical Library

Commander  
U.S. AMC Aberdeen Research & Development Center  
Aberdeen Proving Ground, MD 21005

2 Attn: AMXRD-BD,  
Technical Director

1 Attn: AMXRD-BD,  
Mr. Comer

1 Attn: AMXRD-BD,  
Mr. Grollman

1 Attn: AMXRD-L,  
Technical Library

Commander  
Picatinny Arsenal  
Dover, NJ 07801

1 Attn: Technical Director

1 Attn: Dr. J. Picard

2 Attn: Scientific & Technical  
Information Branch

1 Attn: Dr. Y. Carignan

1 Attn: Dr. D. Downs

1 Attn: Dr. T. Gora

1 Attn: Mr. C. Lenchitz

Commander  
Harry Diamond Laboratories  
Washington, DC 20438

1 Attn: AMXDO-TIB

1 Attn: AMXDO-TD/002

Commander  
Technical Library, Bldg. 313  
Aberdeen Proving Ground, MD 21005

Commander  
U.S. Army Armament Command  
Rock Island Arsenal  
Rock Island, IL 61201

1 Attn: AMSAR-MT,  
Mr. G. Cowan

1 Attn: AMSAR-RDG,  
Mr. S. Spaulding

1 Attn: AMSAR,  
Technical Info Office

1 Attn: AMSAR-KE

1 Attn: AMSAR-RDT

1 Attn: AMSAR-LMC

1 Attn: AMSAR-ASF

1 Attn: AMSAR-RD-G,  
Larry Moore

Commander  
Air Force Armament Laboratory  
Eglin AFB, FL 35242

1 Attn: DLOS

1 Attn: AFATL-DLDG,  
Mr. D. Davis

1 Attn: ADTC-ADLEG,  
Lt. Cook

1 Attn: ADTC (ADBPS-12)

Commander  
Air Materiel Area  
Attn: MMECA  
Hill AFB, UT 84401

Commander  
U.S. Naval Ordnance Laboratory  
Attn: Technical Director  
White Oak, MD 20910

Commander  
U.S. Naval Ordnance Station  
Attn: Technical Director  
Indian Head, MD 20640

Commander  
U.S. Naval Weapons Laboratory  
Attn: Technical Director  
Dahlgren, VA 22448

Commander  
U.S. Naval Air Systems Command  
Attn: AIR-604 (3)  
Washington, DC 20360

Commander  
Watervliet Arsenal  
Attn: Technical Director  
Watervliet, NY 12189

Commander  
Lake City Army Ammunition Plant  
Independence, MO 64056

1 Attn: SARLC-IE  
Quality Assurance Division

1 Attn: SARLC-ATL  
Ammunition Technical  
Laboratory

Commander  
Radford Army Ammunition Plant  
Attn: SMURO-AD, J. Horvarth  
Radford, VA 24141

Commander  
Twin Cities Army Ammunition Plant  
Box 689  
Minneapolis, MN 55440

Commander  
U.S. Army Aviation Systems Command  
Attn: AMSAV-E  
12th & Spruce Streets  
St. Louis, MO 63166

Commander  
U.S. Army Electronics Command  
Attn: AMSEL-DL  
Ft. Monmouth, NJ 07703

Commander  
U.S. Army Tank Automotive Command  
Warren, MI 48090

1 Attn: AMSTA-CL

1 Attn: CDC Liaison Officer

Commander  
U.S. Army Missile Command  
Huntsville, AL 35809

1 Attn: AMSMI-R,  
Dr. J. Merrit

1 Attn: AMSMI-R,  
R. Mitchell

Commander  
U.S. Army Mobility Equipment  
Research & Development Center  
Ft. Belvoir, VA 22060

1 Attn: Technical Document Center,  
Bldg 315

1 Attn: AMSME-RZT

Commander  
U.S. Army Materials & Mechanics  
Research Center  
Watertown, MA 02172

Commander  
Badger Army Ammunition Plant  
Attn: SMUBO-Q, E. Johnson  
Baraboo, WI 53913

Commander  
U.S. Army White Sands Missile Range  
Attn: Technical Library  
NM 88002

Commander  
Edgewood Arsenal  
Attn: SAREA-RB  
Edgewood Arsenal, MD 21010

Commander  
U.S. Army Aberdeen Research & Develop-  
ment Center - BRL  
Aberdeen Proving Ground, MD 21005

1 Attn: BRL,  
Dr. R.J. Eichelberger,  
Director

1 Attn: Dr. Austin Barrows

1 Attn: Dr. Eli Freedman

1 Attn: Dr. Ingo May

1 Attn: Dr. Michael Schroeder

1 Attn: Denis F. Strenzwilk

1 Attn: DR. Kevin White

Commander  
U.S. Army Tropic Test Center  
Attn: STETC-MO-A (Tech Ly)  
Drawer 943  
Ft. Clayton, Canal Zone 07827

Commander  
U.S. Army Research Office (Durham)  
Box CM, Duke Station  
Durham, NC 27706

Commander  
U.S. Naval Ordnance Systems Command  
Attn: ORD-9132  
Washington, DC 20360

Commander  
U.S. Naval Ordnance Laboratory  
Attn: Code 730, Library  
Silver Spring, MD 20360

Office of Vice Chief of Staff  
Department of the Army  
Attn: CSAVCS-W-TIS  
Washington, DC 20310

Commander  
U.S. Naval Weapons Center  
China Lake, CA 93555

1 Attn: J. Sherman

1 Attn: Code 4522

1 Attn: Code 4581

Headquarters  
Defense Atomic Support Agency  
Washington, DC

Headquarters  
USAF (AFCSAI)  
Washington, DC 20330

Advanced Research Projects Agency(2) 1 Attn: AOA-M/107-B  
Department of Defense  
Washington, DC 20301

Director  
U.S. Army Aeronautical Research  
Laboratory  
Moffett Naval Air Station, CA 94035 1 Attn: TD/107-1

Director  
U.S. Army Research Office  
Attn: Library  
3045 Columbia Pike  
Arlington, VA 22204 1 Attn: PD/64-4  
G. White

AFSOR (SREP, Dr. B. Wolfson)  
1400 Wilson Blvd.  
Arlington, VA 22209 1 Attn: MD/220-1  
Mr. S. Miller

Chemical Propulsion Information  
Agency (3) 2 Attn: MDP-R/64-2  
Applied Physics Laboratory  
The John Hopkins University  
Silver Spring, MD 20910 2 Attn: MDP-R/64-2  
M.P. Devine

Director  
Institute for Defense Analyses  
Attn: RESD, Technical Info Office  
400 Army-Navy Drive  
Arlington, VA 22202 1 Attn: MDP-R/64-3  
H. A. Kirshner

Director  
NASA Scientific & Technical  
Information Facility  
Attn: SAF/DL, Acq Div  
P.O. Box 33  
College Park, MD 20470

Dr. Henry Prask  
National Bureau of Standards  
Reactor Radiation Division, Bldg 235  
Washington, DC

Defense Documentation Center (12)  
Cameron Station  
Alexandria, VA 22314

Frankford Arsenal:

3 Attn: TSP-L/51-2  
(1 - Reference copy,  
1 - Circulation copy,  
1 - Record copy)

Printing & Reproduction Division  
FRANKFORD ARSENAL  
Date Printed: 1 August 1975